

Influence of Soil Moisture on Long-Term Sorption of Diuron and Isoproturon by Soil

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Abstract: Long-term sorption of diuron and isoproturon by a clay loam soil was investigated for nine weeks at two herbicide doses (0.6 or 3 mg kg^{-1}) and two soil moisture contents (35 or 62% w/w, i.e. 3.16 or 1 kPa) by measuring changes in herbicide concentrations in the soil solution sampled by means of glass micro-fibre filters in presence of sodium azide ($200 \text{ mg litre}^{-1}$) which inhibited biodegradation for more than four weeks. After the first day equilibration period, where adsorption mainly occurred ($>70\%$ adsorbed), herbicide concentrations in the soil solution decreased (about 50% for diuron; up to 38% for isoproturon) for two weeks but equilibration required about one month. Small amounts of herbicides were sorbed during this process ($<10\%$ of the initial (24-h) adsorption). These were similar for both herbicides, although diuron was initially more adsorbed. Values of the partition coefficients of herbicides between soil and soil solution were increased (75 – 125% for diuron; 29 – 67% for isoproturon). High soil moisture enhanced sorption speed for both herbicides and increased final sorption only for diuron. Sodium azide inhibited long-term sorption of the more stable diuron and this effect was reversed by low temperature only at the low soil moisture. Sodium azide action might be complex (competition, effect on soil micro-organisms) and was not elucidated.

Key words: sorption, herbicide, soil, soil moisture

1 INTRODUCTION

Although adsorption of pesticides by soils is rapid and mainly occurs in a few minutes or hours in slurry condition^{1–3} as well as for undispersed soil,⁴ it has been recognized that this phenomenon requires much longer periods of time to equilibrate. There is some evidence that adsorption of diuron,⁵ imazethapyr⁶ and isoproturon⁷ by undispersed soils continues for days. In slurry conditions, adsorption of atrazine⁸ and alachlor⁹ proceeds for at least three days. Boesten & van der Pas² have suggested that some sorption sites could equilibrate on a time scale of weeks, but experimental measurements are scarce. Long-term sorption kinetics of cyanazine and metribuzin by soil have been evaluated from assessment of soil solution concentrations and soil residues over a 260-day period, but, due to degradation, desorption could occur and then sorption might be also interpreted in terms of hysteresis.¹⁰ Nevertheless they were shown to play a possible significant role in transport of these herbicides in soil, since they improved the

model in which they were incorporated.¹⁰ Because of the lack of knowledge in this field, our aim was to investigate long-term sorption of diuron and isoproturon by an undispersed soil when degradation did not occur. This was achieved by using sodium azide as a biocide to prevent biological degradation¹¹ although this control may be incomplete.¹² Because previous results⁴ suggested that high soil moisture could favour long-term sorption, special attention was given to this factor and the specific effect of sodium azide on sorption was considered for the more stable diuron.

2 MATERIALS AND METHODS

2.1 Soil and chemicals

A sieved (0.5 – 2 mm) air-dried clay loam soil (sand 18% , silt 49% , clay 33% , organic carbon 1.36% , CEC $20 \text{ meq } 100 \text{ g}^{-1}$ and pH 7.9) collected near Dijon (France) was used in this study. Soil moisture content was 5.7% (w/w) on an oven-dry basis and it was determined⁴ to

be 35 and 62% at 3.16 and 1 kPa matrix potential respectively.

[Carbonyl- ^{14}C]diuron (3-(3,4 dichlorophenyl)-1,1-dimethylurea) and [carbonyl- ^{14}C] isoproturon (3-(4 isopropyl-phenyl)-1,1-dimethylurea) were synthesized as described previously⁵ and dissolved in 96% ethanol. The radiolabelled herbicides (99% radiochemical purity) had specific activities of 309 and 337 MBq mmol⁻¹ respectively. Analytical grade compounds (Cluzeau info. labo, Sainte Foy la Grande, France) were also dissolved in ethanol.

2.2 Kinetic study

The sorption kinetics of diuron and isoproturon by the soil were determined at two soil moisture contents and two herbicide doses as previously described.⁴ Soil samples (10 g equivalent dry soil) were placed in 5-cm diameter Petri dishes. Known volumes (2.93 or 5.63 ml) of aqueous solutions of radiolabelled herbicides prepared from the above ethanolic solutions and containing sodium azide (200 mg litre⁻¹) were applied to the soil surface by pipette bringing the soil moisture to the desired value (35 or 62%). Concentrations of solutions were 10.24 or 2.05 mg litre⁻¹ for the low soil moisture and 5.33 or 1.07 mg litre⁻¹ for the high soil moisture, corresponding to 3 and 0.6 mg kg⁻¹ dry soil, respectively. The radioactivity of the solutions was adjusted to provide the same amount of ^{14}C for each sample: 3.4 and 2.1 kBq for diuron and isoproturon respectively. Immediately after treatment, the Petri dishes were weighed, closed with 'Parafilm' (American Can Company, Greenwich, USA) and placed at 18°C. The herbicide concentrations in the soil solutions were determined 1 day, 1, 2, 4, 6 and 9 weeks after treatment in three replicates. At each sampling time, the Petri dishes were weighed to check for the soil moisture. The soil solution was then sampled by means of glass micro-fibre filters (Whatman GF/A) and herbicide concentrations were measured. Briefly, two stacked 42.5 mm diameter filters were laid on the soil surface and a slight pressure was applied for 10 s. The upper moist filter was recovered and weighed in a liquid scintillation counting vial to determine the volume of the collected liquid phase. Then ethanol (2 ml) and scintillation cocktail (15 ml) were added for measurement of the dissolved radioactivity. Herbicide concentration in the soil solution was calculated assuming no degradation.

2.3 Checking for degradation

To confirm that herbicides were not degraded in the soil during the experiment, at each sampling time one soil sample from each condition was suspended in methanol (30 ml) for 10 min and centrifuged (10 min). Supernatant was recovered and extraction was repeated until

^{14}C depletion was complete (typically four times). The radioactivity of the combined extracts was measured by liquid scintillation counting and then extracts were concentrated to a small volume and analysed by HPLC with a Varian 9010 solvent delivery system equipped with a Varian C18 column (ODS-80TM, 4.6 mm ID, 25 cm) and a Berthold radioactivity monitor (LB 507 A). The mobile phase was water + acetonitrile (50 + 50 by volume for diuron and 55 + 45 by volume for isoproturon) at a flow rate of 1 ml min⁻¹. To recover radioactive compounds which might be slowly released by soil, samples were further extracted with methanol (30 ml) for three days and centrifuged and this extraction was repeated twice. The radioactivity of the combined extracts referred to as 'slowly released radioactivity' was determined by liquid scintillation counting and then extracts were concentrated and analysed as above. After extraction, the residual soil samples were air dried and aliquots were combusted in an oxidizer (Packard 306) to determine amounts of unextracted radioactivity.

2.4 Influence of sodium azide

The effect of sodium azide on sorption was assessed for diuron, which was not readily degraded in the soil. The sorption kinetics were achieved as before, at 18°C, two soil moisture contents (35 or 62%), two herbicide doses (0.6 or 3 mg kg⁻¹) and with or without sodium azide for comparison. Diuron concentrations were measured 1, 7 and 14 days after treatment and degradation was checked.

Because sodium azide might influence sorption both directly and indirectly through its effect on microbial growth and activity in the soil, its mode of action was investigated by repeating the above experiment at two temperatures (4 and 18°C) except that diuron was applied at the only low dose and measurements were done 1 and 14 days after treatment.

2.5 Data analysis

Data were submitted to ANOVA¹³ to evaluate effects of the studied factors at $P = 0.05$ and coefficients of variation were calculated.

3 RESULTS

3.1 Degradation

For each herbicide, in the experiment related to kinetic study, the radioactivity extracted from soil samples (expressed as percent of that applied) was similar at both soil moisture contents and pesticide doses and so the corresponding data were averaged for these factors (Fig. 1). For isoproturon, the applied radioactivity was

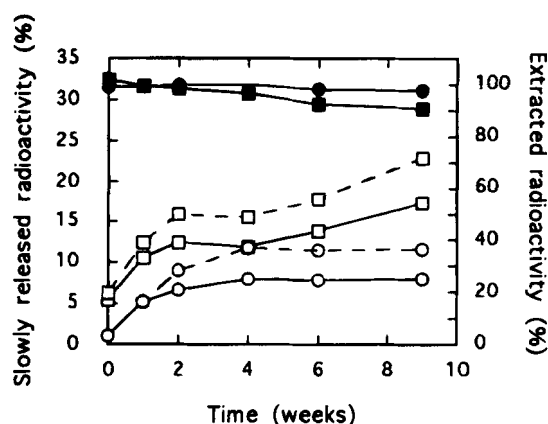


Fig. 1. Radioactivity extracted from the soil after treatment with ^{14}C -labelled (■) diuron or (●) isoproturon (right axis) and radioactivity slowly released by the soil treated with (□) diuron and (○) isoproturon at (---) 0.3 or (—) 6 mg kg^{-1} (left axis). Measurements started 1 DAT.

fully extracted over the experimental period and qualitative analyses revealed a single compound with the same retention time as the parent molecule. A similar pattern was observed for diuron; however, the extracted radioactivity decreased to 90% of the applied ^{14}C within the four to nine weeks' period after treatment, but no degradation product was detected by HPLC. In that case the missing radioactivity was recovered by combustion (data not shown). Because soil moisture had no effect on amounts of slowly released radioac-

tivity, the corresponding data were averaged for this factor (Fig. 1). For both herbicides these amounts were shown to be related to the parent molecules and they increased with time especially over the first two weeks and at the low dose. They were always higher (about twice) for diuron.

In experiments related to sodium azide effect, the radioactivity extracted from soil samples ranged from 96.5 to 100% of that applied and no degradation product of diuron was detected by HPLC (data not shown).

Because degradation products were never detected in soil extracts, radioactivity in the soil solution was attributed to the parent molecules and herbicide concentrations in the soil solution were easily derived.

3.2 Sorption kinetics

As early as one day after treatment (DAT), concentrations of diuron or isoproturon in the soil solution were strongly reduced as compared to the concentrations of the corresponding applied solutions (Fig. 2). They were higher at the high dose and at each dose diuron showed lower concentrations than isoproturon. Whatever the dose and the soil moisture content, concentrations of both herbicides significantly declined after the first day equilibration period. For diuron, concentrations were substantially reduced (46 to 57%), especially over the

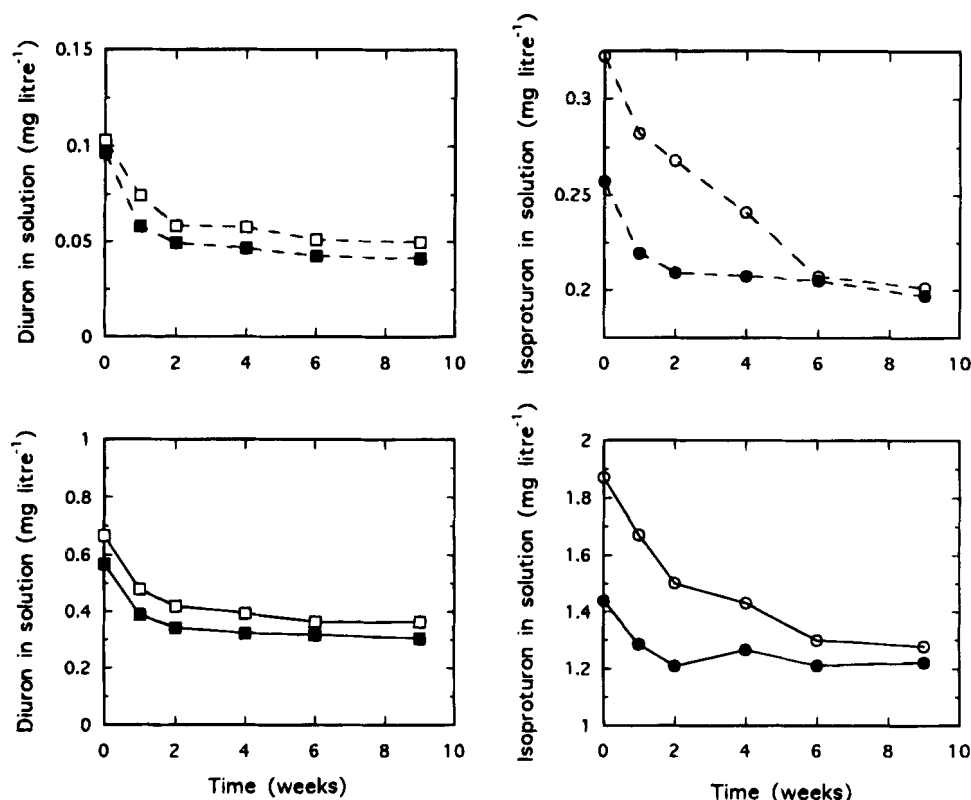


Fig. 2. Changes in (■, □) diuron and (●, ○) isoproturon concentrations in the soil solution after soil treatment with herbicides at (---) 0.6 or (—) 3 mg kg^{-1} and at (□, ○) 35% or (■, ●) 62% soil moisture content. Measurements started 1 DAT. Coefficients of variation ranged from 3.6 to 4.2%.

first two weeks. At both doses, they were significantly higher at the low soil moisture content and differences did not depend on time (no significant interaction). For isoproturon, concentrations showed a less marked decrease as a function of time. At the high soil moisture this decrease was small (15% at the high dose and 23% at the low dose) and it mainly occurred over the first two weeks. At the low soil moisture it was more substantial (32% at the high dose and 38% at the low dose) and more regular over the experimental period. At both doses, concentrations of isoproturon were significantly higher at the low soil moisture but differences disappeared when increasing time (interactions were significant).

Water losses of soil samples were evaluated from weight variations. These losses could reach 6% of the water contained in each sample but they were usually <3% (data not shown) and then they were neglected. Assuming uniform concentration in the soil solution, amounts of herbicides adsorbed by the soil one day after treatment were calculated and expressed as percentages of those applied (Table 1). At that time, more than 70% of the herbicides were adsorbed by the soil. Amounts were higher for diuron and for both herbicides they were higher at the low dose and they decreased as the soil moisture content increased. Amounts of herbicides sorbed by the soil after the first day equilibration period were calculated at each sampling time from the changes in herbicide concentrations in the soil solution without correction for degradation and expressed as percentages of those applied (Fig. 3). These amounts were in the same range for both herbicides, although they were usually slightly higher for isoproturon. They accounted for a small proportion of the applied herbicides (<7%) and they were low as compared to those adsorbed for the first day (<10%). For diuron, in every condition, they significantly increased with time, especially over the first two weeks. They were also significantly higher at the high soil moisture and differences were larger at the low dose (interaction was significant) but herbicide dose had no significant effect. For isoproturon, data showed large variability ($CV = 18\%$).

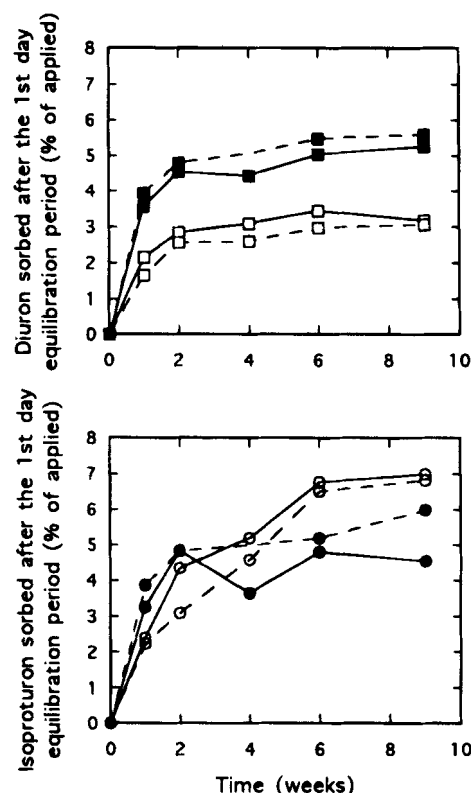


Fig. 3. Amounts of diuron and isoproturon sorbed by the soil after the first day equilibration period. Symbols as in Fig. 2. Coefficients of variation were 7.6 and 18%.

Despite this low accuracy, amounts of sorbed herbicide significantly increased with time, under every condition. Soil moisture and herbicide dose had no significant effect, but interaction between time and soil moisture was significant. Accordingly, the time course changes depended on soil moisture. At the high soil moisture, the observed increase mainly occurred over the first two weeks. At the low soil moisture it was more regular and amounts of sorbed herbicide tended to be initially lower and then to be higher at the end of the experimental period.

Values of the partition coefficients of herbicides between the soil and the soil solution ($\text{mg kg}^{-1}/\text{mg}$

TABLE 1
Amounts of Herbicides Adsorbed by the Soil after the First Day Equilibration Period

Herbicide	Dose (mg kg^{-1})	Amounts adsorbed (% of applied) Soil moisture content (%)	
		35	62
Diuron	0.6	94.1	90.2
	3	92.5	88.6
Isoproturon	0.6	81.9	74.3
	3	78	70

Effects of herbicide, dose and soil moisture content were significant ($CV = 0.7\%$).

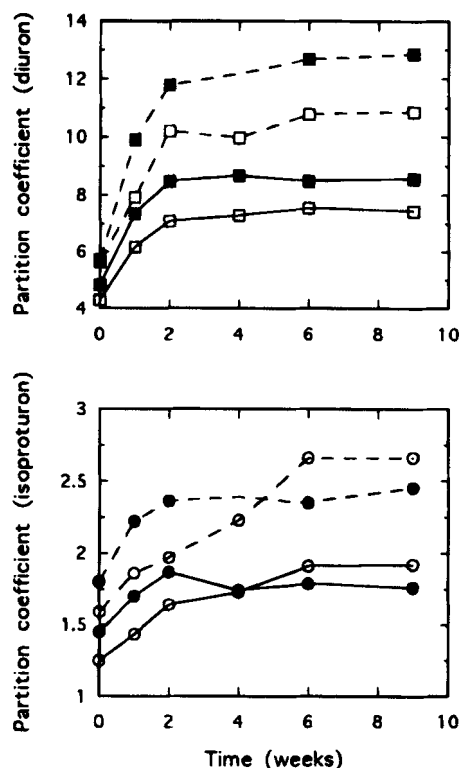


Fig. 4. Changes in values of the partition coefficients of diuron and isoproturon between soil and soil solution after soil treatment with herbicides. Symbols as in Fig. 2. Measurements started 1 DAT. Coefficients of variation were 2.7 and 4.8%.

litre) were calculated at each sampling time, taking into account the possible degradation of diuron in the soil after one month. Results are presented in Fig. 4. Values were much higher for diuron and for both herbicides they were significantly higher at the low dose. For diuron, under every condition, values of the partition coefficient significantly increased with time (75 to 125%) especially over the first two weeks before reaching a plateau. At both doses, they were significantly higher at the high soil moisture and the difference increased with time (interaction was significant). For isoproturon, values of the partition coefficient also significantly increased with time, but that was less important (29 to 67%). At both doses, soil moisture had a significant effect and the significant interaction between time and soil moisture evidenced that time course changes depended on soil moisture. At the high soil moisture, increase mainly occurred over the first two weeks, while it was more regular at the low soil moisture. Under that condition, values of the partition coefficient were initially lower then they were higher at the end of the experimental period.

3.3 Sodium azide effect

Under every condition, diuron concentrations in the soil solution were significantly higher in presence of

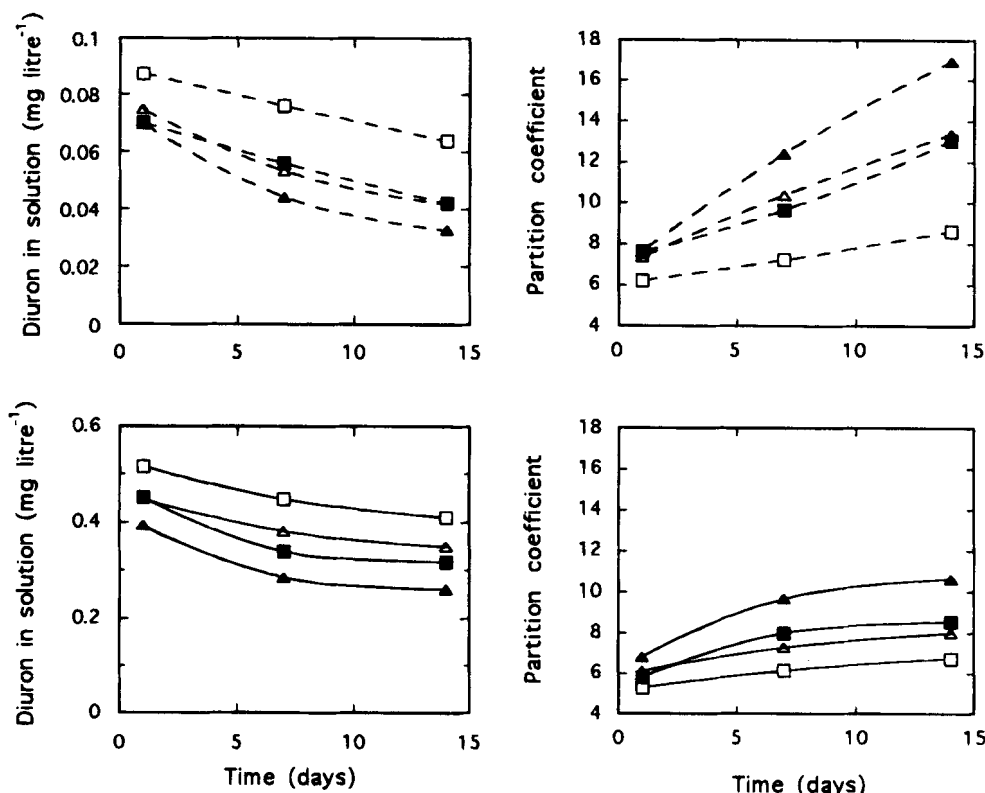


Fig. 5. Influence of sodium azide on diuron concentrations in the soil solution and on diuron partition between soil and soil solution. Soil was treated with herbicide at (---) 0.6 or (—) 3 mg kg⁻¹ and (■, □) with or (▲, △) without sodium azide at (□, △) 35% or (■, ▲) 62% soil moisture content. Coefficients of variation ranged from 2.2 to 4.6%.

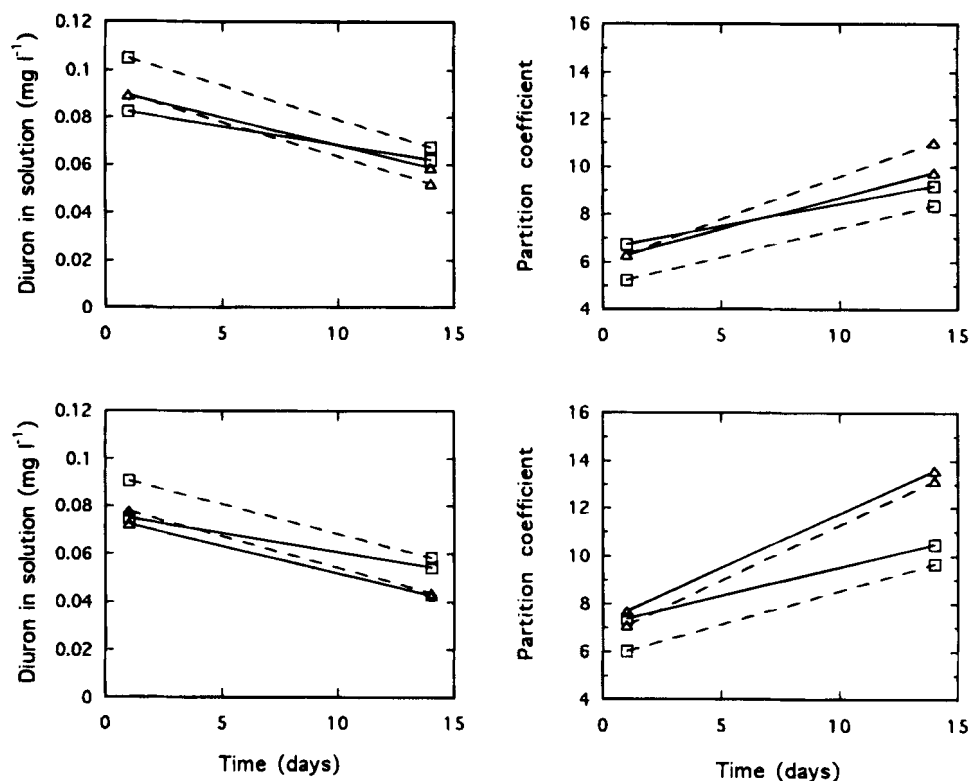


Fig. 6. Influence of temperature on sodium azide effect on diuron concentration in the soil solution and on diuron partition between soil and soil solution. Soil was treated with diuron (0.6 mg kg^{-1}) at 35% (top) or 62% (bottom) soil moisture content and (\square) with or (\triangle) without sodium azide at (---) 18 or (—) 4°C . Coefficients of variation ranged from 4 to 4.5%.

sodium azide and values of the partition coefficient were lower (Fig. 5). Significant interactions showed that, in most cases, differences increased with time. At both soil moisture contents, decreasing temperature significantly reduced diuron concentrations in the soil solution (Fig. 6) but this effect tended to disappear as time increased (interactions were significant). Sodium azide had a significant effect and significant interaction with temperature at the low soil moisture showed that temperature only inhibited the sodium azide effect under that condition (Fig. 6). At the high soil moisture, decreasing temperature significantly increased values of the partition coefficient and the significant effect of sodium azide did not depend on temperature (no significant interaction). At the low soil moisture, temperature had no significant effect, but the significant effect of sodium azide depended on temperature (interaction was significant). Under that condition, decreasing temperature cancelled the sodium azide effect.

4 DISCUSSION

Sodium azide completely prevented degradation of isoproturon, which has been shown to be readily degraded in this soil,⁷ and thus microbial degradation of this

herbicide¹⁴ is confirmed. This effect was less clear for diuron, which might be either degraded or partly extractable beyond a one-month residence time in the soil. However, results demonstrated that, in the presence of sodium azide, both herbicides were not degraded and were fully extractable for at least one month after soil treatment, and then any changes in herbicide concentration in the soil solution might be attributed to the sorption process. They also suggest that bound residues do not form as long as degradation does not occur. Time-course changes in amounts of slowly released radioactivity suggest that the herbicides became less easily extractable with increasing residence time in the soil. This phenomenon did not depend on soil moisture, but it was more important for herbicides at the low dose.

Adsorption of diuron and isoproturon mainly occurred for the first day, in accordance with previous results⁴ but the significant decrease in herbicide concentrations in the soil solution after the first day equilibration period provides strong evidence for long-term sorption of both herbicides by the soil. This phenomenon occurred mainly in the first two weeks, but true equilibrium might be achieved within approximately one month, as previously observed for isoproturon under different conditions.⁷ It might result from diffusion of herbicides into small pores of the soil and/or diffusion into the soil organic matter matrix as dis-

cussed by Brusseau *et al.*^{15,16} So far the relationship between long-term sorption and soil texture, including soil organic matter, has mainly been investigated over short periods of time.³ Our results suggest that it is worth carrying out experiments over longer periods.

Small amounts of herbicides were sorbed during the long-term sorption process (<10% of the initial (24-h) adsorption); however, due to the small volumes of soil water, this was enough to substantially decrease herbicide concentrations in the soil solutions and to increase values of the partition coefficients of herbicides between the soil and the soil solution. It is expected that such observations would be more difficult to gain in slurry condition using smaller soil samples and larger amounts of water phase, and the experimental technique used in this study should provide some advantages in this respect. Although diuron was initially (24 h) more adsorbed and thus was less abundant in the soil solution, the amounts of diuron and isoproturon sorbed by the soil after the first day equilibration period were similar. Accordingly, it is believed that long-term sorption is herbicide-type-dependent. Because amounts of sorbed herbicides, expressed as percentages, were the same at both doses, for each herbicide, long-term sorption might be roughly proportional to herbicide dose.

Results clearly show that soil moisture may influence long-term sorption kinetics and sorption equilibria but these effects depend on the herbicide. For diuron, long-term sorption was more rapid and the final sorption was higher at the high soil moisture, which might favour diffusion of this herbicide into the soil and ensure better contact between the herbicide and sorbent surfaces of soil components. For isoproturon, effects were more complex: high soil moisture might enhance sorption speed (although this effect was less clear than for diuron) but did not favour the final sorption. Our results do not allow an explanation of this particular behaviour of the herbicide in the soil.

It is worth noting the inverse relationship between long-term sorption of the herbicides and changes in their extractability. However, because herbicide dose and soil moisture had different effects on these phenomena, they might be unrelated.

Because diuron was not degraded and was fully extractable from soil treated with herbicide alone, the influence of sodium azide on sorption could be seen from direct comparison of diuron concentrations in the soil solution and of the corresponding values of the partition coefficient. Results clearly demonstrated an inhibitory effect of sodium azide on long-term sorption. This might be due to direct physicochemical interactions, such as competition, or result from inhibition of soil micro-organisms capable of taking up pesticides^{17,18} and/or modifying soil organic matter and its adsorbent properties. The fact that low temperature, which is likely to reduce microbial growth, did not suppress the effect of sodium azide at the high soil moisture favours

the physicochemical hypothesis, but because of reversed results at the low soil moisture, the mode of action of sodium azide is still uncertain. However, it is thought that long-term sorption was underestimated in presence of sodium azide.

5 CONCLUSIONS

Using sodium azide to prevent biodegradation of diuron and isoproturon in soil and glass microfibre filters to sample soil solution for herbicide concentration assessment allowed the long-term (> 24 h) sorption of these herbicides by soil to be studied under realistic conditions. Long-term sorption is evident and equilibration requires approximately one month. Small amounts of herbicides are sorbed during this process but they are enough to reduce concentrations in the soil solution and to increase values of the partition coefficients between soil and soil solution. Long-term sorption depends on the herbicide, and soil moisture content appears to be an important factor. High soil moisture enhances sorption speed but its effect on final sorption depends on the herbicide. Sodium azide inhibits long-term sorption. This effect may be complex and is not elucidated.

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